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DIELECTRIC ABSORPTION AT 3 cm. IN SOME HIGHER ALKYL PHENOLS

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(*Received December*, 13, 1963)

ABSTRACT. Dielectric measurements have been carried out on para-octyl, -nonyl and -dodecyl phenols in solution in benzene at 3.22 cm. and at a radio frequency of 1 mc/sec. From the measurements at 3.22 cm. using a single frequency method, the relaxation time and the dipole moment have been determined for these molecules and from the radio frequency measurements, dipole moments have been deduced for the same molecules. The results are reported and discussed.

INTRODUCTION

A programme of work on quantitative determinations of dielectric absorption, in particular, at microwave frequencies, of some molecules has been undertaken in this laboratory with a view to studying dielectric dispersion in these molecules and testing the existing theories of electric polarization and molecular structure from such studies. As a first step in this programme, a study of dielectric absorption in some alkyl phenols has been taken up, since for these molecules no studies of dielectric absorption particularly at microwave frequencies seem to have been carried out so far, as far as the authors are aware. The present investigation reports the results of dielectric measurements in solution in benzene at 3.22 cm and at a radio frequency of 1 mc/sec. carried out under this programme, on three higher alkyl phenols, namely, para-octyl, -nonyl and -dodecyl phenols, and the values of relaxation times and dipole moments determined for these molecules.

METHOD

Dielectric measurements at 3 cm.

In the wave-guide standing wave method (Roberts and Von Hippel, 1946; Dakin and Works, 1947; Surber Jr. and Crouch Jr, 1948; Heston Jr, and others, 1950) the inverse voltage standing wave ratio (VSWR) E_{min}/E_{max} exhibits (Von Hippel, 1954) maxima for sample lengths of odd multiples of $\lambda_d/4$ with short circuit termination, λ_d being the guide wavelength in the dielectric filled section of the guide and for low loss media such as dilute solutions of a polar substance in a non-polar solvent, the magnitudes of these maxima increase with the number of the odd multiple. This makes the other losses small compared

to the dielectric loss of the sample, and therefore it is possible to determine the dielectric loss more accurately. As the rate of shift of the first minimum point in air with sample length is maximum in this region, it will be fairly easy to locate the positions of these maxima rather precisely. Another advantage of taking measurements on odd multiples of sample lengths is that computations of ϵ' and ϵ'', the dielectric constant and loss factor respectively, become much simplified.

The real part of the dielectric constant, ϵ' is given by the equation

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \left[1 - \left(\frac{\alpha_d \lambda_d}{2\pi}\right)^2\right] \quad \ldots (1)$$

where

α_d = attenuation resulting from dielectric power loss.

λ_c = cut-off wave-length.

and λ_0 = free space wave-length.

For low-loss media, such as dilute solutions of a polar substance in a non-polar solvent, this equation reduces to

$$\epsilon' = \left(\frac{\lambda_0}{\lambda_c}\right)^2 + \left(\frac{\lambda_0}{\lambda_d}\right)^2 \quad \ldots (2)$$

An experimental determination of λ_d, together with a knowledge of λ_0 and λ_c will yield ϵ' from the above equation for low-loss media.

The loss factor, ϵ'' is given by the relation

$$\epsilon'' = \frac{1}{\pi}\left(\frac{\lambda_0}{\lambda_d}\right)^2 \alpha_d \lambda_d \quad \ldots (3)$$

The inverse VSWR, ρ_n at the n-th maximum produced by a short circuited low-loss dielectric filled section, may be expressed as

$$\rho_n = \left(\frac{\lambda_g}{\lambda_d}\right) \cdot n \cdot (\alpha_d + \alpha_c)\frac{\lambda_d}{4} + R_{sc}\left(\frac{\lambda_g}{\lambda_d}\right)^2 \quad \ldots (4)$$

where α_c = attenuation resulting from power loss in the walls of the dielectric section of the wave-guide,

R_{sc} = the per unit resistance of the terminating plunger referred to the air-filled guide,

λ_g = guide wave-length in the air-filled section

and n = an odd integer.

R_{sc} may be determined either from calculated power loss or from the characteristic impedance of the metal. Using this value of R_{sc} and experimentally determined

value of ρ_n and the equation given above, the total attenuation $(\alpha_d+\alpha_c)$ can be determined. From this and a preliminary determination of α_c, α_d can be obtained which when substituted into equation (3) will yield ϵ''. However, in the present work, the total attenuation $(\alpha_d+\alpha_c)$ is obtained from the slope of the plot of ρ_n versus 'n', as this procedure eliminates the resistance of the plunger, R_{sc}.

Determination of relaxation time and dipole moment

A single frequency method for solutions due to Gopalkrishna (1957) has been used for the determination of the relaxation time 'τ' and the dipole moment 'μ'. In this method, for determining 'τ, a plot is made between

$$x = \frac{\epsilon'+\epsilon'^2+\epsilon''^2-2}{(\epsilon'+2)^2+\epsilon''^2}$$

and

$$y = \frac{3\epsilon''}{(\epsilon'+2)^2+\epsilon''^2}$$

the slope of which yields $\frac{1}{\omega\tau}$, ω being the angular frequency. For the determination of 'μ', a graph between x and W, the weight fraction, is plotted, the slope of which would be equal to

$$\frac{4\pi N\mu^2}{9kTM} \cdot \frac{1}{1+\omega^2\tau^2} \cdot d_0$$

where N is the Avagadro's number

k = the Boltzman constant

T = absolute temperature

M = Molecular weight of the solute

and d_0 = density of the solvent.

Determination of 'μ' from Radio Frequency Measurements.

Guggenheim's modified method (Guggenheim, 1949; 1951) is used for the determination of the dipole moment. In this method

$$\mu = 0.0128\sqrt{P_0\overline{T}}$$

where

$$P_0 = \frac{3}{(\epsilon_1+2)^2} \cdot \frac{M_2}{d_1} \cdot \Delta$$

where

$$\Delta = \left(\frac{\epsilon_{12}-\epsilon_1}{W_2}\right)_{W_2\to 0} - \left(\frac{n^2_{12}-n^2_1}{W_2}\right)_{W_2\to 0}$$

ϵ_1 = dielectric constant of the solvent

ϵ_{12} = dielectric constant of the solution

M_2 = Molecular weight of the solute

d_1 = density of the solvent

W_2 = weight fraction of the solute

n_{12} = refractive index of the solution

n_1 = refractive index of the solvent.

Δ is determined from the difference of the intercepts of the plots $\left(\frac{\epsilon_{12}-\epsilon_1}{W_2}\right)$ and $\left(\frac{n^2_{12}-n^2_1}{W_2}\right)$ against W_2.

EXPERIMENTAL

3 *cm.equipment* : A block diagram of the experimental set-up for dielectric measurements at 3 *cm.* is shown in Fig. (1). All the components in the unit except the *E*-plane 90° bend, liquid absorption cell and galvanometer, are of

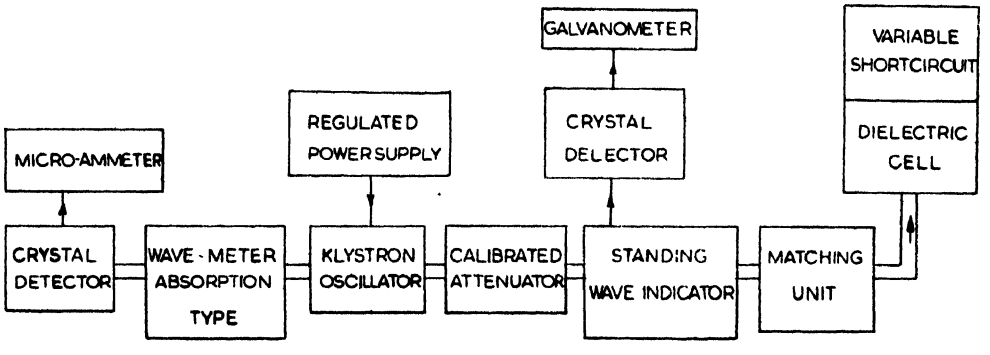

Fig. 1. Block diagram of the 3 cm. set-up

Scanners Ltd., London. *E*-plane 90° bend was fabricated by us and was found to have an inverse VSWR of 0.96 at 9295 mc/sec., the frequency at which the measurements were carried out. The dielectric absorption cell, also fabricated by us, consisted of a standard $1'' \times 1/2''$ O.D. $\times 0.050''$ wall, rectangular brass waveguide of length 6" silvered inside and was provided with a non-contact shorting plunger driven by a micrometer screw of traverse 4" and of least count (1/2000)". The galvanometer used was a low period one with a resistance of 450 ohms and had a sensitivity 2,000 m. per microampere at 2 meters scale distance. The accuracy of the probe displacement along the slotted line of the standing wave indicator used was 0.002 cm.

The unit was operated in the H_{01} mode. To provide adequate decoupling of the klystron, attenuator was set at a value greater than 10db. The standing

wave-indicator crystal was calibrated and found to obey the square law. A matching unit was used in between the slotted section and the cell to match out any possible reflections from the bend and the mica window and it was adjusted for the standing wave ratio to be very nearly equal to unity with a dummy load.

Radio frequency set-up : This set-up consisted of a Franklin oscillator (Le Fevre and others, 1950) oscillating at 1 mc/sec., which was coupled to a crystal controlled wave meter. The oscillatory circuit of the former included a dielectric cell and a precision condenser of Muirhead Co., England, with a total capacity of 250 pf and with a precision of 0.025 pf, all arranged in parallel. Grid tuned circuit of the wavemeter consisted of a stable 500 pf, variable condenser and a one-megacyle quartz crystal, all connected in parallel. The operation of the set-up was as described in the literature.

The experimental cell used is similar to that designed by Sayce and Briscoe (1925) and modified by Sugden (1933) and is described in the literature. The cell was silvered using the method recommended by Sugden. The deposition was found to be satisfactory only when the two solutions used in the silvering process were cooled to a temperature of about 10°C or lower, mixed and then transferred to the cell, instead of mixing and transferring them at the room temperature 27°C±1°C. The capacity of the cell was 52.56 pf.

Measurements. The three phenols *p*-octyl, -nonyl and -dodecyl were supplied by Rohm and Hass Co., U.S.A. They were distilled twice at low pressure (*p*-octyl phenol 146-47°C/8 mm. Hg; *p*-nonylphenol−165 −67°C/4 mm.Hg, and *p*-dodecylpenol -186-87°C/4 mm.Hg) and rejecting the initial fractions, the fractions that distilled at the temperatures given above were collected. *p*-octyl phenol was a white flaked solid and the other two phenols were clear liquids. Analar benzene was used as the solvent. Before use it was dried over sodium wire and distilled under anhydrous conditions. Five to six solutions of each of the phenols after double distillation were prepared in conical flasks of 50 c.c. with ground glass stoppers and were studied immediately.

At 3 cm : The dielectric constant and the loss of the solvent benzene were measured at a frepuency of 9295 mc/sec. ($\lambda_0 = 3.22$ cm) and at the room temperature 27°C±1°C. They were respectively 2.270 and <0.001. For each solution six to seven successive maxima of inverse VSWR 'ρ_n' at the frequency and at the temperature mentioned just above, were located and measured. The maximum VSWR occurs for an electrical length very close to an exact resonant length. This would be the case for an electrically long low loss sample. Therefore, although six to seven maxima of VSWR 'ρ_n' were measured, λ_d was actually determined from the measurements on the higher resonant lengths only, namely, the 15th, 13th and 11th. From each of these higher resonant lengths $\lambda_d/4$ was determined and from these a mean value for λ_d was obtained. This procedure adopted in evaluating λ_d enables changes of the order of 0.002 cm. in λ_d (this amounted to

a change of 0.004 in the value of ϵ') to be determined. Using this average value of λ_d, ϵ' was determined from equation (2) given earlier. As for ϵ'' it can be seen from equation (4) the graph between 'ρ_n' and n (odd integer) is a straight-line whose slope will yield $(\alpha_d+\alpha_c)$ and whose intercept on the ρ_n axis will give the plunger resistance. Such plots are shown in fig. 2 for the different solutions

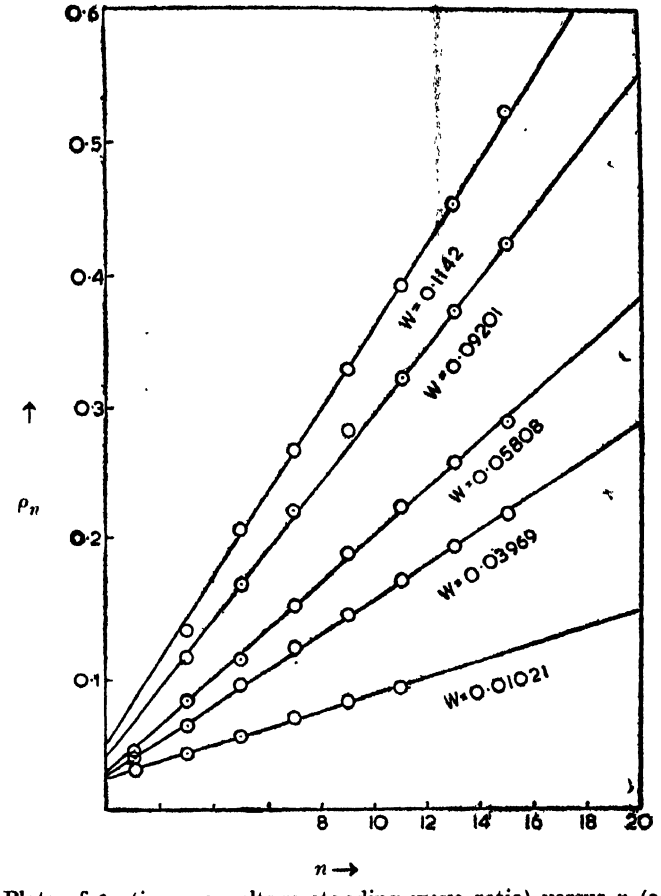

Fig. 2. Plots of ρ_n (inverse voltage standing wave ratio) versus n (odd integer) for different weight fractions of dodecyl phenol.

of dodecyl phenol. α_c was found to be very small. Therefore, in the actual determination of ϵ'' using equation (3) total attenuation was used instead of α_d and this did not introduce any significant error.

At Radio frequency: Dielectric constant ϵ_1 of benzene and that for the various solutions ϵ_{12} was determined using the radio frequency set-up already described by finding the capacity of the cell with and without the substance. The dielectric constant of benzene at 27°C±1°C was 2.264. Refractive indices for the various solutions and for the solvent benzene were determined for the sodium D lines using a Pulfrich refractometer. The refractive index of benzene at 27°C±1°C was measured to be 1.49412.

RESULTS

The ϵ' and ϵ'' values determined at 3 cm. for the different solutions of each of the three phenols are given in tables, I, II and III. In these tables, the first column gives the weight fraction of the solute the second ϵ' and the third ϵ'' while in the fourth and the fifth columns are given values of x and y needed in the determinations of 'τ' and 'μ'. The values of ϵ' are estimated to be accurate to within 0.5% and those of ϵ'' to within 2%. From these ϵ' and ϵ'' values, τ and μ were determined for the three phenols as indicated earlier and are given in table IV. The density of the solvent, benzene was taken to be 0·87901 gm/c.c.

TABLE I

p-Octyl phenol

W	ϵ'	ϵ''	x	y
0.02298	2.286	0.01345	0.3002	0.002197
0.03897	2.297	0.01874	0.3018	0.003039
0.05788	2.313	0.02879	0.3045	0.004647
0.06766	2.320	0.03599	0.3057	0.005786
0.08855	2.332	0.04262	0.3077	0.006797
0.1298	2.353	0.06610	0.3112	0.010440

TABLE II

p-Nonyl phenol

W	ϵ'	ϵ''	x	y
0.009279	2.286	0.008245	0.3002	0.001347
0.02773	2.301	0.01408	0.3022	0.002279
0.04444	2.309	0.02136	0.3039	0.003449
0.06270	2.320	0.02590	0.3056	0.004882
0.08095	2.320	0.03683	0.3056	0.005928
0.11400	2.332	0.04682	0.3077	0.007484

TABLE III

p-Dodecyl phenol

W	ϵ'	ϵ''	x	y
0.01021	2.282	0.007457	0.2994	0.001220
0.03969	2.290	0.01569	0.3007	0.002556
0.05808	2.295	0.02218	0.3015	0.003606
0.09201	2.304	0.03157	0.3030	0.005112
0.1142	2.309	0.03904	0.3041	0.006303

TABLE IV

Molecule	μ in Debye units	τ in $\mu\mu$ sec.
p-Octyl phenol	1.37±0.10	11.0±2.0
p-Nonyl phenol	1.37±0.10	12.4±2.0
p-Dodecyl phenol	1.19±0.10	18.4±2.0

Plots of x against y and x against w are shown for dodecyl phenol in fig. 3 for the purpose of illustration.

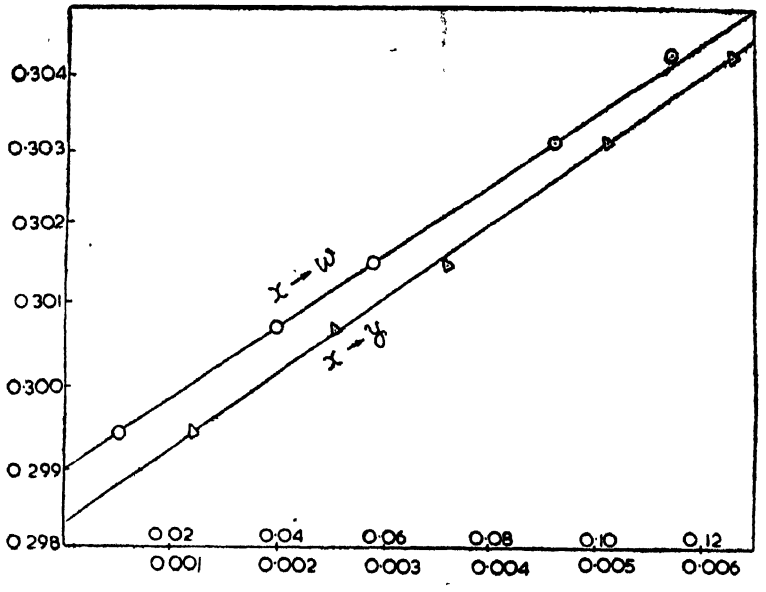

Fig. 3. Plots of x versus y and x versus W the weight fraction.

Tables V, VI and VII give the radio frequency values of ϵ_{12} and n_{12} for different solutions of each of the three phenols together with the value of μ of each molecule determined as outlined earlier.

TABLE V

p-Octyl phenol

Wt. fraction W_2	Dielectric const. of the solution ϵ_{12}	Refractive index of the solution n_{12}
0.008050	2.277	1.49459
0.01414	2.287	1.49459
0.02708	2.306	1.49483
0.03926	2.320	1.49493
0.05893	2.348	1.49511
0.08166	2.380	1.49535
	$\mu=1.53\pm0.03$ *D*	

TABLE VI
p-Nonyl phenol

Wt. fraction W_2	Dielectric const. of the solution ε_{12}	Refractive index of the solution n_{12}
0.01414	2.283	1.49445
0.02516	2.297	1.49459
0.04982	2.335	1.49487
0.06671	2.354	1.49501
0.08971	2.382	1.49516
	$\mu = 1.59 \pm 0.03$ *D*	

TABLE VII
p-Dodecyl phenol

Wt. fraction W_2	Dielectric const. of the solution ε_{12}	Refractive index of the solution n_{12}
0.01504	2.281	1.49421
0.04182	2.308	1.49418
0.05478	2.323	1.49459
0.07394	2.342	1.49489
0.09574	2.373	1.49510
	$\mu = 1.58 \pm 0.03$ *D*	

Plots of $\frac{\varepsilon_{12}-\varepsilon_1}{W_2}$ versus W_2 and $\frac{n^2_{12}-n^2_1}{W_2}$ versus W_2 are given in fig. 4 for dodecyl phenol for the sake of illustration.

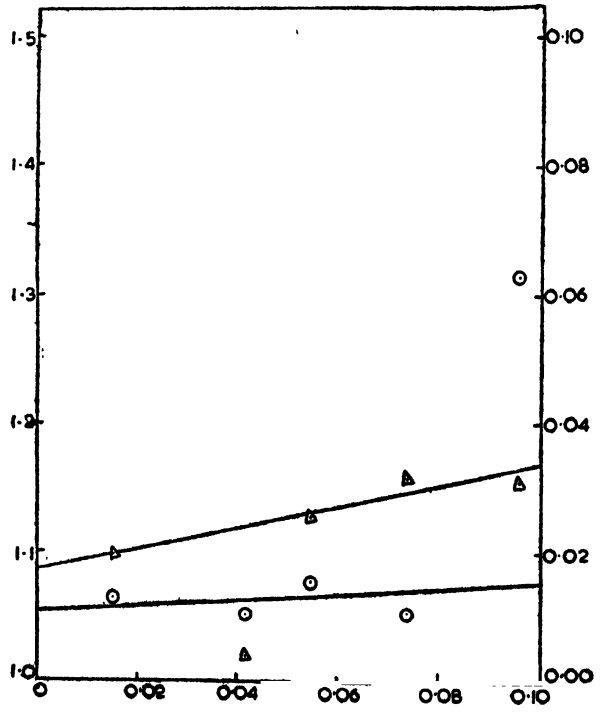

Fig. 4. Plots of $\frac{\varepsilon_{12}-\varepsilon_1}{W_2}$ and $\frac{n^2_{12}-n_1{}^2}{W_2}$ versus W_2 the weight fraction shown by O and Δ respectively.

The limits of accuracy of both the relaxation times and the dipole moments of these molecules have been arrived at from the results of several independent sets of measurements on each molecule.

DISCUSSION

The three molecules studied in this investigation are members of a homologous series. The dipole moments of these molecules determined in this work indicate that they are approximately equal. Two values for the dipole moment of phenol in benzene solution have been reported in the literature; one of them is around 1.45D (Boud, and others, 1955; Lumbroso and Dumas, 1955; Katagiri, 1950) and the other around 1.6D (Donle and Gehrckens, 1932; Bottcher 1952; Smyth, 1955; Kimura and Fujishiro, 1959, and Goode and Ibbitson, 1960). The radio frequency values determined by us for these molecules in benzene solution are close to one another and to the literature value for phenol, 1.6D. We have carried out dielectric measurements at 1 cm. too, on these three phenols in benzene solution (unpublished) and have evaluated both τ and μ for them, using the data at 3 cm., and 1 cm, and using a double frequency method of Whiffen and Thompson (1946). These values are in fair agreement with those at 3 cm., determined using a single frequency method already described. Both the microwave value of μ are rather close to the other literature value for phenol in benzene solution, namely, 1.45D. Whatever may be the true value of the dipole moment of phenol in benzene solution, that is whether it is close to 1.6D or to 1.45D, the fact that the dipole moments of these molecules are approximately equal, whether we consider our radio frequency values or our microwave values, may indicate that the dipole moments of these phenols depend mainly on that of the OH group and little on that of the alkyl group.

There is, however, some divergence between the microwave values of μ and the radio frequency values, reported in this investigation. It may be partly accounted for as follows : The accuracy we have attained in our measurements of ϵ' and ϵ'' is of the order of magnitude that is normally employed for dielectric measurements at 3 cm. Values of ϵ' of a solution determined for different lengths of the solution in the cell have been found to agree to within 0.5% and those of the loss factor, ϵ'' to within 2%. For these molecules which are higher members of a series with rather high molecular weights, the variation in ϵ' with concentration has been found to be so small that, although detectable, it almost lies within the limits of error of measurements. That this reason may partly explain the discrepancy between the microwave and the radio frequency value of the dipole moment seems to be confirmed by our preliminary results on the same isomer of the lower phenols of the series, namely *p*-ethyl, -propyl and -butyl phenols. For these molecules the variation of ϵ' with concentration has been found to be comparatively larger and the same degree of accuracy in the dielectric measurements

at 3 cm., has led to values of μ for these lower phenols in fair agreement with the radio frequency values. However, we feel that the divergence between the radio frequency and microwave values in these higher phenols are more than could be attributed to this factor only. Further it may also be mentioned that similar discrepancies between the radio frequency values and those determined at microwave frequencies have also been reported in the literature in the case of a few other molecules.

With regard to the relaxation times of these molecules, it has not been possible to determine them more accurately for reasons mentioned above. But, yet the values seem to be of the right order of magnitude. It may be noted that they increase from octyl to dodecyl phenol as they should, in accordance with theory, because the relaxation time of a molecule depends upon the size of the molecule. To test this point further, a study of temperature variation of dielectric absorpion of para-dodecyl phenol at 3 cm., has been undertaken and our preliminary results indicate that this molecule has a relaxation time in benzene solution at room temperature, around the value at 3 cm., reported above. Similar studies of temperature variation of dielectric absorption on the other two phenols also are in progress.

Investigations of dielectric absorption at microwave frequencies on some other phenols are in progress.

ACKNOWLEDGEMENT

One of the authors (G.C.H.) wishes to express his grateful thanks to the Ministry of Scientific Research and Cultural Affairs, Government of India, for the award of a Scientific Research Training Scholarship, during the tenure of which this work was mostly carried out. We are also thankful to Dr. S. Munavalli for having made available to us the samples of phenols used in this work.

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